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COMPUTER CONTROLLED QUALITY OF ANALYTICAL MEASUREMENTS

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COMPUTER CONTROLLED QUALITY OF ANALYTICAL MEASUREMENTS

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ABSTRACT

A PDP 11/35 computer system is used in evaluating analytical chemistry measurements quality control data at the Barnwell Nuclear Fuel Plant. This computerized measurement quality control system has several features which are not available in manual systems.

These features include such items as real-time measurement control, computer calculated bias corrections and standard deviation estimates, surveillance applications, evaluation of measurement system variables, records storage, immediate analyst recertification, and the elimination of routine analysis of known bench standards.

The effectiveness of the Barnwell computer system has been demonstrated in gathering and assimilating the measurements of over 1100 quality control samples obtained during a recent plant demonstration run. These data were used to determine equations for predicting measurement reliability estimates (bias and precision); to evaluate the measurement systems; and to provide direction for modification of chemistry methods. The analytical chemistry measurement quality control activities represented 10% of the total analytical chemistry effort.

OVERVIEW OF THE MEASUREMENT SYSTEMS

A PDP 11/35 computer system has been used to automate an analytical chemistry laboratory measurement quality control program at the Barnwell Nuclear Fuel Plant in Barnwell, South Carolina.(1) The program was set up to determine the reliability, i.e., precision and accuracy, of the measurements generated by the analytical chemistry laboratory personnel and to identify measurements of Quality Control Standards that exceed the control limits.

The Barnwell Nuclear Fuel Plant was built to recover uranium and plutonium from spent light water reactor fuel. When the plant is operated at capacity, 800 analytical chemistry measurements will be required per day. Chemical analyses of process streams and plant products are necessary for controlling processes, calibrating in-line monitors, and obtaining nuclear materials accountability measurements. The quality of these measurements is of utmost importance.

The Nuclear Regulatory Commission requires a "Measurement Control Program for Special Nuclear Materials Control and Accounting" as specified in (10 CFR 70.57). The Barnwell program satisfies all of the requirements of this regulation and has been expanded to include all routine analytical chemistry measurements.

The computer system used in the laboratory is shown in Figure 1. It consists of a PDP 11/35 central processing unit with 128K of memory, multiple disk drives, dual magnetic tape transports, and various input-output terminals. Of the five million words of disk storage, one quarter is used for the quality control program activities. Data from the analyzed standards are transferred periodically to magnetic tape for long-term storage. Terminals are located at strategic points in the laboratories, process control room, and administrative building. Currently, a mass spectrometer, a multichannel analyzer, density meters, and fluorophotometers are interfaced directly to the computer system. The computer system has been operating successfully for three years. During this period, less than 1% unscheduled downtime has been experienced. The system is built around the RSTS/E (Resource Sharing-Time Sharing) operating system version 6B and utilizes a BASIC PLUS language processor. All application programs for the individual analytical chemistry methods are written in a modular format using this powerful version of BASIC. During a recent eight-week demonstration run, 12,000 measurements were made on over 5,000 samples by laboratory personnel. An evaluation of these measurements is discussed in the last section of this paper.

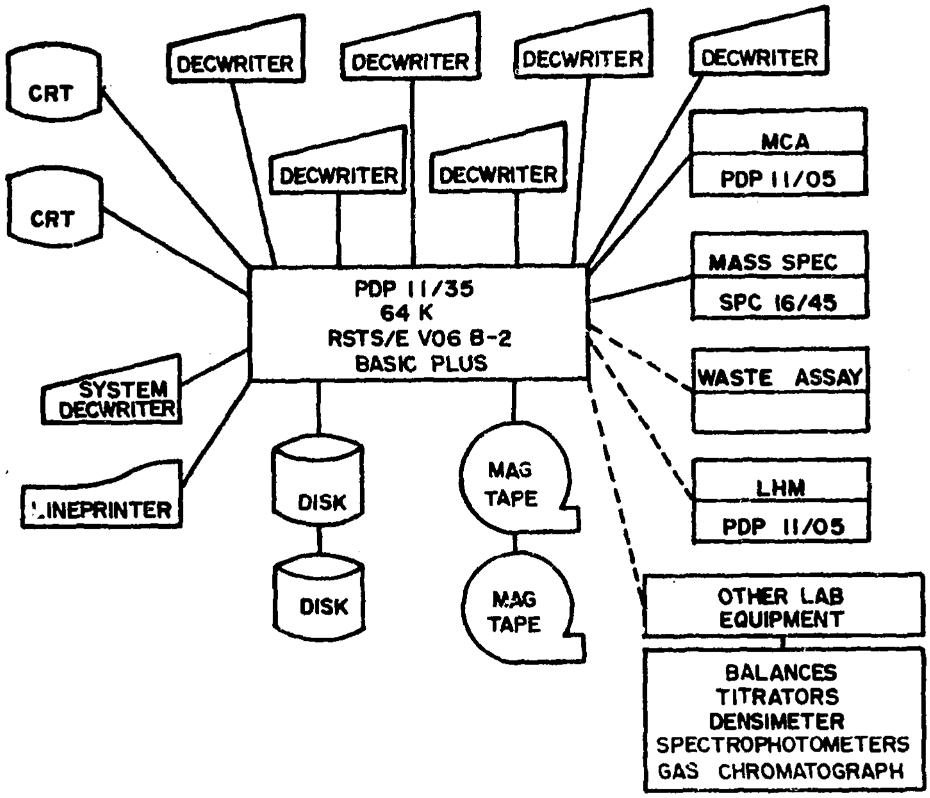

FIGURE 1 — SCHEMATIC SHOWING THE COMPONENTS OF A LABORATORY COMPUTER SYSTEM.

OBJECTIVES OF THE MEASUREMENT QUALITY CONTROL PROGRAM

The two major objectives are measurement reliability and measurement control. In the analytical laboratory a measurement is defined as a determination of mass, volume, quantity, composition, or other property of a material. This determination is made by using a measurement system. Its elements are the analyst, procedure, laboratory equipment, reagents, standards, calibration curve, and computational system. These elements are considered variables in the measurement determination. Changes in these variables cause uncertainty in the measurements. This uncertainty or error can be defined as any discrepancy between the computed, observed, or measured quantity and the true, specified, or theoretically correct value of that quantity.

Statistical methods programmed into the computer system are used to quantify the measurement error. The statistics calculated are referred to as reliability statistics. One of these terms is accuracy, a qualitative term used to describe the agreement between the expected value of a measurement and the true value. The better the agreement, the greater the accuracy. The second term used in discussing reliability statistics is precision, a qualitative term used to describe the internal consistency of repeat measurements without regard to whether or not they are centered around their "true" value. A measurement may be precise; that is, it can be reproduced or repeated fairly consistently, yet it may not be accurate. It may be in poor agreement with the true value.

When the accuracy and precision of a measurement system has been determined it is possible to work at controlling the variables in the measurement system. Laboratory management will adjust or develop a measurement system until it produces measurements of desired quality. A three standard deviation control limit has been established for all routine measurement systems.

Quality control standards are analyzed using the measurement system until enough data are obtained to calculate the accuracy and precision. These data are grouped for each standard and their means and variances are calculated. The variances are then fitted to one of four models by standard regression techniques to obtain a fit which smooths the variances as a function of each standard's known value. This equation is used to predict the variance for a measurement. A second regression is made to establish a bias correction prediction equation, which is a function of the reported value and is inversely weighted according to the previously calculated variances. Both first and second degree polynomials are used. The variance statistics are used to set the control limits. Future measurements of these quality control standards must fall within a three standard deviations limit or the measurement system is determined to be out of control.

The laboratory computer system has been used to automate this control function for the analytical chemistry measurement processes. The computer calculates and evaluates the quality control standards measurements and provides real-time measurement control. If a result is out of control, the computer will not accept sample data for the analytical chemistry method until the faulty element in the measurement system is corrected.

OPERATIONS OF THE COMPUTER SYSTEM

In a plant where over 200 samples are taken daily during full operation, computer applications play an important role in obtaining operating efficiency. Analytical chemistry measurement activities use five major computer system functions. These are listed below:

1 Communications: Process operators request sampling and analyses on batches of various plant materials via the terminals located throughout the plant. Approved analytical chemistry measurements are printed on the control room terminals.

2. Records: After the requests are received, analytical records are created in the computer. Each request is given an identifying log number, so that it can be traced by both the batch identification number and the log number. Work sheets specifying the analyses required are printed for the analysts by the computer.

3. Calculations and Data Evaluations: Several pieces of laboratory equipment are interfaced directly to the computer. This feature saves time and eliminates transcription errors. Several Mettler/Parr Density Meters are interfaced. The density measurement system includes a density meter, water bath, digital thermometers, and interface equipment as shown in Figure 2.

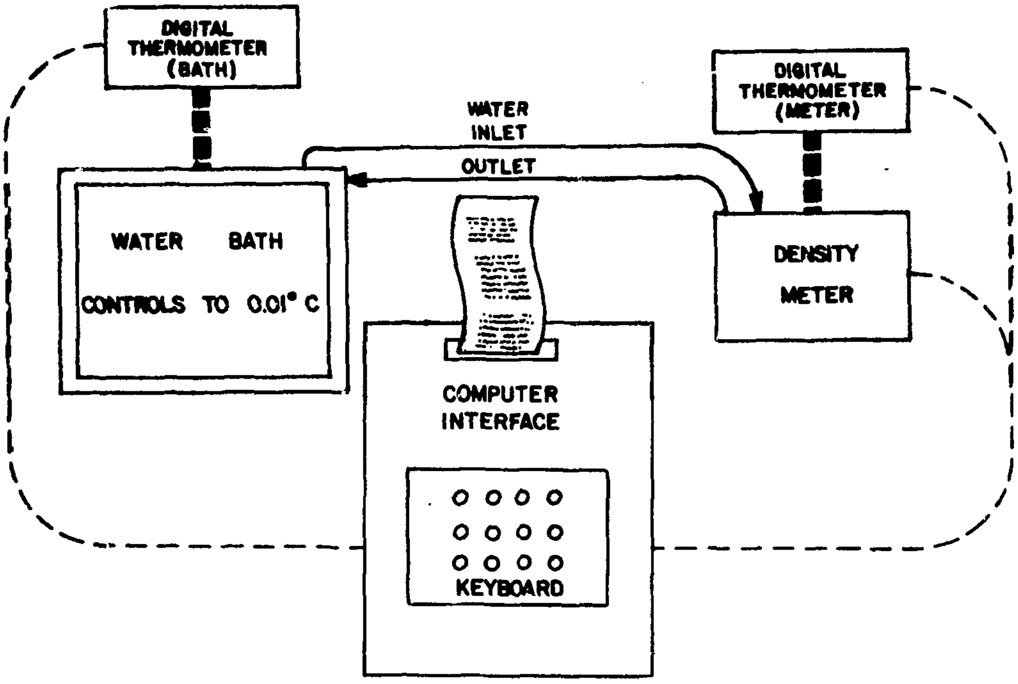

FIGURE 2 -- SCHEMATIC OF DENSITY MEASUREMENT SYSTEM

The analyst is required to type information on the interface keyboard, as requested by the computer. If he does not correctly respond to the computer's request, the sample measurement is not completed. Table I shows the dialogue between the analyst using the density measurement system and the computer.

TABLE I

DIALOG BETWEEN AN ANALYST AND A COMPUTER INTERFACED TO A DENSITY METER

Computer Printout	Analyst Input	
	DATA	Program called up
08-JAN-79, 14:43		Date/Time
CREW/ANALYST?	B/732	Crew/Employee Number
METHOD?	DN-DM-1-A	Density method
INSTRUMENT A, B, C, D, E?	E	DMA-55 instrument
CALIBRATE?	N	Not done routinely
LAST CONSTANT = .170043 E-3		
QC OR SPL?	SPL	Analyst specifies
NO QC RUN YET THIS SHIFT		Program locked out
QC OR SPL?	QC	Control is specified
QC NUMBER?	2DNØ1533	ID from label
TEMPERATURE?	25.01	Manual input in °C
DEN, PER, CONC?	DEN	Density reading specified
INTRODUCE SAMPLE		Measuring cell filled
TYPE Y WHEN READY	Y	After cell is filled
EQUILIBRATING?		Temperature being adjusted
DEN (Ø) .99684		Interface reads the instrument signals, prints the densities
DEN (Ø) .99688		
DATA		Measurement starts
DEN (1) .99688		Nine readings taken at specified intervals and printed
DEN (n) .99691		
DEN = .99689		Average density
@ 25 DEG C		Temperature
RESULTS OK (Y OR N)?	Y	Results approved
RESULTS IN LIMITS		Measurement - OK
	-- OR --	
"QC SPL OUT OF LIMITS, ANALYZE ANOTHER STANDARD"		System out of control

Computer programs have been written for each analytical chemistry method to calculate the measurement result using input from the analyst. The analyst must approve the calculation before the result is stored in the computer record and communicated to the requestor.

Process samples and quality control standards have specification parameters or control limits for each measurement point. The computer compares the measurement with the appropriate parameters or limits and prints out its evaluation for the analyst. This feature allows the analyst, supervisor, and requestor to know how the sample or standard compares to the specified parameter or control limits.

If the measurement made on the quality control standard exceeds the control limits, the calculation program will not accept the data used to calculate plant sample measurements. The analyst must check the components of the measurement system and correct any that are abnormal, then analyze another standard. Two criteria must be satisfied before the plant samples can be analyzed.

a. A quality control standard must be analyzed each eight-hour shift, before plant samples are analyzed.

b. The standard's measurement must be within the control limits.

This function provides real-time measurement control.

4. Measurement Reliability: Provisions are made in each calculation program to correct each measurement for the average measurement system bias and to calculate the standard deviation. This is accomplished by using the equations derived from the statistical evaluation of data obtained from the last 100 quality control standards, as described in the fourth paragraph of the preceding section. This application of the quality control program reliability statistics provides measurements that have been bias corrected for systematic error and an estimate of the random analytical measurement error.

5. Reports: In addition to reporting the results to the requestor's terminal, hard copy reports are generated by the computer system on the line printer. These reports give all of the pertinent measurement information, such as analyst, date, method, bias corrected measurement, standard deviations, and units. An example of one of these reports is shown in Table II, below.

TABLE II

ILLUSTRATION OF COMPUTER PRINTED FINAL REPORT OF ANALYTICAL MEASUREMENTS

FINAL REPORT -- SAMPLE 11157

Sample Point: N-34

Sample ID: QC 32

REQUESTED BY AS/JPC — APPROVED BY JDS

LOG IN 15-SEP-78, 15:33 — LOG OUT 15-SEP-78, 23:10

SAMPLING DATE 9-15-78 15-SEP-78 — SAMPLING TIME 15:33

COMMENT
U-VI REQUESTED AND RUN
SMALL AMOUNT OF SAMPLE DID NOT TITRATE ENOUGH

ANALYSIS	RESULT	UNITS	SD (1SIGMA)	METHOD	ANALYST	DATE	TIME
U	0.5	G U/L	0.03	U-VI-1-A	C/LAK	15-SEP-78	18:10
H	3.623	N	0.07	ACID-VP-1-B	C/LAK	15-SEP-78	20:06
DN	1.1222	G/ML	0.0006				
		AT 25 DEG C		DN-DM-1-A	C/LAK	15-SEP-78	20:20

The Standards Laboratory personnel of the Analytical Services Department are responsible for the implementation and administration of the measurement quality control program. They prepare the standards and reagents needed for each measurement system. They monitor the measurement systems and maintain all of the quality control records.

Surveillance of the measurement quality control program activities has been simplified by using the laboratory computer system for the following four functions:

1. Organization: The computer is used to organize the standards for each method and to store all identification information from a minimum amount of input from the chemist. Two or three different sublevels of standards are prepared for each of four or five concentration levels covering the range of a method. The computer provides a listing of a sequence of identification numbers for the standards and alters the levels and sublevels to minimize analysts bias when the standards are analyzed. The sequencing assures that each level is measured an equal number of times. The sequence number, reference value, and standard deviation are stored in the computer.

2. Label: The computer also prints labels containing an acronym to identify the method and the sequential number. These labels are placed on the flame-sealed ampuls of standards for the method.

3. Surveillance: The quality control chemist is able to check the status of the standards upon command from any terminal. An example of the measurements made using a fluorophotometric method is shown below in Table III. A status of all standards analyzed during the previous 24 hours is printed out daily on the standards laboratory terminal. These data are reviewed to monitor the methods currently being used.

TABLE III

COMPUTER PRINTED STATUS OF ANALYZED QUALITY CONTROL STANDARDS

QC STATUS (Chemist Call-Up Program)

? ACRONYM = 2U02 (Chemist Specifies Method and Instrument Acronym)

2U02

STD #	REF	EXP	BIAS	SD	IN/OUT	DEVIATION	C/A DATE
501	1.00	1.15	.15	0.1	IN	1.5	E/JAL 27-JAN-79
502	1.1	1.05	-.05	0.1	IN	-0.5	A/CJA 31-JAN-79
503	13.0	15.8	2.8	1.3	IN	2.15	E/JAL 03-FEB-79
504	12.7	15.2	2.5	1.3	IN	1.92	B/LAK 06-FEB-79
505	56.0	62.0	6.0	2.5	IN	2.4	E/JAL 07-FEB-79
506	58.5	66.5	8.0	2.5	OUT	3.2	E/JAL 07-FEB-79
90005	30.0	36.0	6.0	1.5	OUT	4.0	E/JAL 07-FEB-79
90006	30.0	29.0	1.0	1.5	IN	-0.33	E/JAL 07-FEB-79

4. Computation: Each month the plant is operated, all of the measurements of the quality control standards are statistically evaluated by the computer. The means for all the experimental data and their associated standard deviations are calculated for each standard. Equations are determined for predicting bias corrections and estimating the standard deviation for each measurement by least squares regression analysis. Other computations are made to determine each analyst's measurement capabilities and to compare the measurement system's performance with the statistics from the preceding evaluation.

Additional measurement quality control program activities will be computerized in the future.

OBSERVATIONS OF A PROGRAM DEMONSTRATION

The measurement quality control program has been tested during a plant demonstration Over an eight-week period. nearly 12,000 measurements were made. Of this total 1.165 were quality control standards.

These measurements were made by analysts having limited experience with the measurement systems. The table below indicates the analysts improved their measurement capabilities as they gained experience. During the first period, 17% of the standards were out of control. By the third period they had improved 30% by dropping their out-of-control percentage to 12%.

TABLE IV

SUMMARY OF QUALITY CONTROL STANDARDS ANALYZED FROM AUGUST 1 THROUGH SEPTEMBER 30(2)

Time	Total Quality Control Standards	Out-of-Control Number	Out-of-Control Percent
1-AUG to 31-AUG	626	105	17%
1-SEP to 15-SEP	294	41	14%
16-SEP to 30-SEP	245	29	12%
TOTAL	1.165	175	15%

The Barnwell program requires one standard be analyzed each shift a method is used. Manual systems require a bench standard having a known reference value be analyzed by the analyst to check out the method. Additional unknown standards are routinely analyzed to provide data free from analyst bias, for determining the random analytical measurement error. The analyst may rationalize that he can use a method even if the bench standard is a little out of the control limits. There is no physical control over the measurement process. The automated program has eliminated the necessity of running more than one standard if the method is in control. The computer evaluates the measurements to provide real-time measurement control. The actual analytical effort expended in measurement quality control has been about 10%. Future use of the computerized measurement control program may reduce this percentage over extended periods of operation.

This computerized methods quality control program has provided an assurance that the methods measurement systems are functioning satisfactorily within prescribed limits before they are used. It provides an instant recertification program for the analyst, as he demonstrates his performance each time he analyzes a quality control standard. This system has proven to be influential in stimulating improvements in analysts measurement capabilities.

SUMMARY

By using a PDP 11/35 computer system to generate analytical records, provide assurance that measurement systems are in statistical control, assimilate data. calculate measurements, apply reliability statistics, evaluate results, and issue final reports. it is possible to produce reliable analytical chemistry measurements in an efficient and economical manner. The operation of the Barnwell computerized measurement quality control program requires about 10% of the analytical laboratory personnel's effort.

REFERENCES

(1) J. P. Clark and G. A. Huff, "Analytical Chemistry Measurements Quality Control Program Using Computer Applications," NBS PUB-528.

(2) J. P. Clark, G. A. Huff, L. G. Jordan, and G. D. Workman, "Analytical Laboratory Support Services for the 1978 Uranium Run," AGNS-1040-2.5-54.

KEYWORDS: Computer control; measurement quality; real-time quality control; and reliability.

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